Proceedings of the American Academy of Arts and Sciences

Vol. 71, No. 6—January, 1937

AN EXPERIMENTAL STUDY OF THE ABSOLUTE TEMPERATURE SCALE. II

THE REPRODUCIBILITY OF THE SULPHUR POINT. THE EFFECT OF PRESSURE ON THE SULPHUR POINT

By James A. Beattie, Manson Benedict, and B. Edwin Blaisdell

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 372.)

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Received August 4, 1936. Presented December 9, 1936.

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1. Introduction

In 1927 the Seventh Conference of Weights and Measures adopted[1] for international use a practical scale of temperature, the International Temperature Scale, °C. (Int.), which was designed to agree as closely as possible with the absolute scale. The international scale is based on a number of reproducible equilibrium temperatures to which numerical values are assigned; and on the indications, computed from certain formulae, of standard interpolation thermometers which are to be constructed and calibrated at the fixed points in a specified manner.

One of the basic fixed points is the temperature of equilibrium between liquid sulphur and its vapor under a pressure of one standard atmosphere (the so-called sulphur boiling point or sulphur point) to which was assigned the value 444.6° C. (Int.). The formula proposed for expressing the equilibrium temperature t_p in degrees C. (Int.) as a function of the vapor pressure p in standard mm. of mercury over the range 680 to 780 mm. of mercury is

$$t_p = t_{760} + 0.0909\,(p - 760) - 0.000048\,(p - 760)^2, \qquad (1)$$

[1] G. K. Burgess, Bur. Standards, J. Research, **1**, 635 (1928).

where t_{760} is the equilibrium temperature at one standard atmosphere pressure.

One standard atmosphere was defined as the "pressure due to a column of mercury 760 mm. high having a mass of 13.5951 g./cm.^{3}, subject to a gravitational acceleration of 980.665 cm./sec.^{2} and is equal to 1,013,250 dynes/cm.^{2}" We shall interpret this definition to mean: (1) one standard atmosphere is the pressure due to a column of mercury 760 mm. high at 0° C. and subject to the standard gravitational acceleration of 980.665 cm. per sec.^{2}; (2) the average density of a column of mercury 760 mm. high in vacuo at 0° C. and standard gravity is 13.5951 gm. per cm.^{3}; and (3) the product $76 \times 13.5951 \times 980.665$ is to be rounded off at 1.013250×10^6. We shall further define one standard millimeter of mercury to be 1/760 standard atmosphere.

In the range from 0° to 660° C. the international temperature t is to be computed from the resistance R_t of a standard platinum resistance thermometer by means of the equation:

$$R_t = R_0 (1 + At + Bt^2), \tag{2}$$

where the constants R_0, A, and B are determined by calibration at the ice, steam and sulphur points. It is usual to write this equation in the Callendar form

$$R_t = R_0 \left[1 + \alpha t - \alpha\delta \frac{t}{100}\left(\frac{t}{100} - 1\right)\right], \tag{3}$$

or

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) \tag{4}$$

$$= t_{pt} + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) \tag{5}$$

where the "platinum temperature" t_{pt} is defined by the linear relation

$$t_{pt} = \frac{R_t - R_0}{\alpha R_0}. \tag{6}$$

In the above equations R_0 is the resistance of the thermometer at the ice point (0° C.),

$$\alpha = A + 100\, B = \frac{R_{100} - R_0}{100\, R_0} \tag{7}$$

is determined from the resistance R_{100} of the thermometer at the normal steam point (100° C.), and

$$\delta = -\frac{B \times 10^4}{A + 100\,B} = \frac{1}{4.446 \times 3.446}\left[444.6 - \frac{R_{444.6} - R_0}{\alpha\, R_0}\right] = \frac{444.6 - t_{pt(444.6)}}{4.446 \times 3.446} \quad (8)$$

is determined from the resistance $R_{444.6}$ of the thermometer at the normal sulphur point (444.6° C. Int.).

The specifications concerning the construction of a standard platinum resistance thermometer may be summarized as follows: the platinum wire should not be smaller than 0.05 mm. or larger than 0.2 mm. in diameter and must be so mounted as to be subject to a minimum of mechanical constraint in order that expansion and contraction accompanying changes of temperature may impose a minimum of mechanical strain on the wire. The portion whose resistance is to be measured shall consist only of platinum and shall be at the uniform temperature which is to be measured. After completion the thermometer should be annealed at a temperature of at least 660° C. The purity and physical condition of the platinum should be such that the ratio R_t/R_0 shall not be less than 1.390 for $t = 100°$, and not less than 2.645 for $t = 444.6°$.

For the purpose of standardizing platinum resistance thermometers at the sulphur boiling point, there were drawn up specifications relating to: (1) the purity of the sulphur, (2) the boiling apparatus, (3) the radiation shield, and (4) the procedure.

(1) The sulphur should not contain over 0.02% of impurities.

(2) The boiling tube should be of glass, fused silica, or similar material, not less than 4 cm. nor more than 6 cm. internal diameter, and must have a free opening at the top for equilibration of pressure. The source of heat and all good conducting material in contact with it must terminate at least 4 cm. below the free surface of the liquid sulphur. Above the source of heat the tube should be surrounded with insulating material; and the vapor column must be sufficiently long so that the top of the radiation shield is not less than 6 cm. below the top of the insulating material surrounding the tube.

(3) The radiation shield should consist of a cylinder, open at the lower end and provided with a conical portion at the top to fit closely to the protecting tube of the thermometer, ample space being provided between the cylinder and the cone for free circulation of the vapor. The cylinder should be 1.5 to 2.5 cm. larger in diameter than the protecting tube of the thermometer, at least 1 cm. smaller in diameter than the inside of the boiling tube, and should extend at

least 1.5 cm. beyond each end of the thermometer coil. The inner surface of the shield should be a poor reflector.

(4) During the standardization of a thermometer, the condensation line of the sulphur should be at least 1 cm. above the top of the insulating material. The calibration is made by taking simultaneous observations of resistance and barometric pressure. The temperature indicated by the thermometer should be independent of vertical displacements of the thermometer and shield.

These specifications follow closely those laid down by Mueller and Burgess[2] who made a comprehensive study of the sulphur point.

Improvements in the construction of platinum resistance thermometers and in the purity of platinum wire due largely to the work done at the U. S. Bureau of Standards have made it possible to measure temperatures with a precision of 0.002° C. or better. Since the sulphur point is one of the basic fixed points on the International Temperature Scale, it seemed desirable to investigate the conditions under which it can be reproduced to 0.002° C. and to check Eq. (1) for the effect of pressure on the equilibrium temperature.

By use of the apparatus shown in Figs. 1 and 2 we have been able to calibrate a platinum resistance thermometer at the sulphur point with a probable error in the value of δ of 0.000 10 units which corresponds to about 0.0017° C. at 444.6° C. Rather wide variations in the conditions of rate of heating, depth of immersion of the thermometer, shielding, temperature of the insulating unit, and diameter of the boiling tube have no effect greater than 0.002° C. on the indicated temperature corresponding to a given pressure. Over the pressure range 660 to 860 mm. the effect of pressure on the sulphur point is given by the relation

$$t_p = 444.6 + 0.0908028\,(p - 760) - 0.000\,047573\,(p - 760)^2 + 0.000\,000\,04361\,(p - 760)^3$$

where t_p is on the international scale. The average deviation of 37 determinations made with two thermometers and two barometers is less than 0.002° C.

2. Apparatus and Materials

Thermometry. Two 25-ohm platinum resistance thermometers[3] of the four lead potential type were used. Thermometer No. 107 was

[2] E. F. Mueller and H. A. Burgess, J. Am. Chem. Soc., **41**, 745 (1919).

[3] For details of construction, see J. A. Beattie, D. D. Jacobus, and J. M. Gaines, Jr., Proc. Am. Acad. Arts and Sci., **66**, 167 (1930).

a Bureau of Standards strain-free type; No. 308 was a Callendar mica-cross type, also of strain-free construction. For each thermometer the ratio R_t/R_0 was greater than 1.392 for $t = 100°$ and greater than 2.653 for $t = 444.6$.

The thermometers were filled with pure, dry nitrogen at a pressure of about 2/3 atm. at room temperature; and annealed by alternate treatment in a molten bath of a eutectic mixture of lithium, sodium and potassium nitrates at about 500° C. and in liquid air. When thermometers are annealed at 660° C. some dehydration of the mica occurs which makes the support friable; and such thermometers do not hold their calibration in the range 0° to 450° C. any better, if as well, as those annealed at the lower temperature.

Resistances were measured on a Mueller type resistance bridge thermostated at 30 ± 0.005° C. All resistances larger than 0.1 ohm were sealed in brass. The distance from the galvanometer mirror to the scale was 4 meters and a change of 0.0001 ohm (approximately 0.001° C.) in the bridge setting caused a deflection of about 6 mm. of the hair line on the scale. The bridge was connected to the commutator by short lengths of No. 3 gauge copper wire. The selector built to accommodate twenty resistance thermometers was similar to that described before[3] except that mercury cups were used instead of binding-posts.

Comparator and Scale. The two-meter Société Genevoise comparator had an invar bar to which the two telescope carriages were keyed and to which the telescopes could be rigidly clamped by means of split collars with tightening screws. The comparator was so placed in relation to the scale and barometer that one turn of the micrometer drum of the filar eye-piece corresponded to exactly 1 mm. (± 0.001 mm.) on the scale. Thousandths of millimeters could be read by estimation of tenths of divisions on the drum.

The invar scale was graduated into fifths of millimeters and ruled to be correct at 20° C. It was calibrated at the U. S. Bureau of Standards. The filar micrometer was always run over all divisions within a distance of 1 mm. of those used. Discrepancies greater than 0.002 mm. have seldom been found.

The comparator and scale hung from universal joints attached to heavy H-beams and were held at the bottom in adjustable bearings. The bottoms of the H-beams were bolted to heavy slate blocks fitted with leveling screws, and the tops were attached to a steel frame-work (bolted to the concrete ceiling beams) by means of an adjustable bearing which held the H-beams permanently in alignment.

The bar of the comparator was made vertical by sighting on three plumb lines 120° apart with one telescope at the top and one at the bottom. The scale was not out of vertical by as much as 0.4 mm., as determined by plumb lines.

The scale was illuminated by means of spot lights, attached one to each telescope carriage, which were turned on only during the reading of the scale. The rulings appeared light on a dark background. The two telescopes agreed on the reading of the same mercury surface to within 0.002 mm.

Barometer. In order to reproduce the sulphur point to within 0.001° C. it is necessary to control and measure the barometric pressure to 0.01 mm. of mercury. By means of the barometer and manostat shown in Fig. 1 pressures in the neighborhood of 1 atmosphere could be controlled to 0.01 mm. for a period of several hours, and read with an average deviation from the mean of 0.002 mm.

The barometer was constructed in duplicate. Its working ranges consisted of 12 cm. lengths of soft glass tubing, 32 mm. internal diameter. The tubes after being mounted in the housing were tested for optical defects. A piano wire 0.2 mm. in diameter was stretched approximately horizontally behind the tubes. The difference between the apparent elevation of the wire at the axis of the tubing and the mean of its elevations at each side represents the distorting effect of the front and back surfaces of the tubing. Over the working range no apparent displacement of the wire greater than 0.005 mm. was found. No correction was applied for this effect.

The upper and lower tubes of each barometer were mounted rigidly with axes vertical and in the same line and were connected with 8 mm. glass tubing. The upper tubes were connected to a common charcoal trap and a MacLeod gauge. The barometer vacuum was checked at intervals; the pressure recorded by the MacLeod gauge was always less than 0.001 mm. When the charcoal trap was cooled in liquid air the mercury height in the barometer was changed less than 0.003 mm. No correction was applied for these effects. The lower tubes of the barometer were connected through stopcocks to a filter and thence to the manostat. The lower tubes were evacuated when the barometer was not in use.

The barometers were enclosed in a brass housing equipped at the front and back with plate-glass windows. The temperature was measured by means of three mercury-in-glass thermometers which had been calibrated against platinum resistance thermometers. The room was thermostated to $\pm$ 1° C. and the air mixed by a blower which

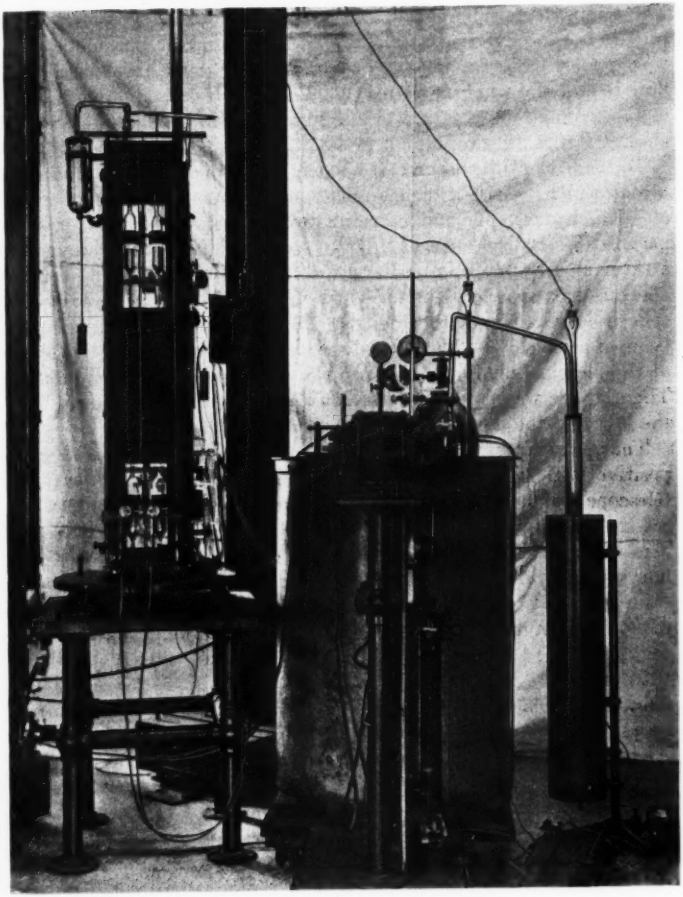

FIGURE 1. Photograph of the apparatus.

drew air from the bottom and delivered it at the top of the room. The temperature difference in the room from top to bottom was 0.1 to 0.2° C.; the difference from top to bottom in the barometer case was at most 0.05° C., and the change in temperature from the beginning to end of a run was at most 0.02° C. An uncertainty of 0.1° C. in the average temperature of the barometer introduces an error of about 0.001° C. in the sulphur point.

To the back of the barometer housing was attached the illuminating device which consisted of a carriage moving on two vertical pieces of ½ inch drill rod, and carrying two optical trains one for each barometer. In each optical train a 6-volt flashlight bulb illuminated a sheet of thin paper immediately in front of which was a circular aperture 1/32 inch in diameter which was at the focus of a compound spherical lens of 5 cm. focal length. The system produced a circular beam of parallel light 23 mm. in diameter which passed over the center of the mercury meniscus and into the telescope of the comparator.[4] The carriage was balanced by a counterweight and was moved from the lower to the upper mercury surface as needed.

The optical train was adjusted so that the beam of light had a small positive angle with respect to the sensible horizon as follows: the telescope was leveled and the cross hair of the filar micrometer was set so that it passed through the mechanical axis of the telescope. The whole telescope was then moved up or down so that the cross hair rested on the mercury meniscus. The zenith angle of the optical train was adjusted until the shadow of the crest of the meniscus on a white card immediately in front of the objective fell slightly above the axis of the telescope.

In order to define each mercury surface more sharply brass shields painted flat black and shaped to fit the back half of the barometric tubes were pressed against the tubes by means of springs. These shields were lowered between the mercury surface and the light source by means of counterweights until the lower edge of the shield was about 0.2 mm. above the crest of the meniscus.

The room was darkened when the barometer was being read so that no light came from the front of the mercury column.

It was found that the height of a mercury surface could be read with an average deviation of 0.002 mm. and that the reading was independent within limits of the lateral displacement of the optical train, the azimuthal angle of the light beam, the angle of the light

[4] See S. C. Collins and B. E. Blaisdell, Rev. Sci. Instr., **7**, 213 (1936). With tubes of large diameter the use of a spherical lens is permissible.

beam to the horizon (provided the beam sloped upward from the optical train) and the height of the shield above the crest of the mercury surface.

No effect was found when the plate-glass window in the front of the barometer was turned top to bottom, or right side to left side.

The barometric fluid was mercury which had been purified by electrolysis in a dilute solution of nitric acid and distilled three times, twice in a current of air at 25 mm. pressure and once in vacuo.

Three of the series of measurements of the effect of pressure on the sulphur point were made with the right hand barometer; one with the left hand barometer. No consistent differences between the results could be found.

Manostat. If the boiling tubes were attached directly to the barometer, the pressure would vary due to slight fluctuations in the height of the vapor column of the boiling fluid, and to variations in temperature of the permanent gas which transmits the pressure to the barometer. It is common practice in precise work to use some kind of ballasting device to control and keep constant the pressure. Our manostat consisted of a 90-liter constant volume steel vessel equipped at the top with two outlets, one of which was connected to the boiling tube and the other to the lower arm of the barometer. The vessel was kept at a temperature of about 30° C. and was thermostated to $\pm$ 0.0005° C. in a constant temperature bath of kerosene. The temperature control was effected by means of a platinum resistance thermometer and a thyratron control circuit.[5] The whole apparatus rested on anti-vibration rubber mountings.

The manostat, sulphur boiling tube and barometer were filled with dry nitrogen or dry helium. Helium was used because it also served for taking the steam point. If air is used oxidation of the sulphur takes place which, in addition to other disadvantages, causes the pressure to drop continually.

The manostat held the pressure constant to within 0.01 mm. for several hours. The pressure did not fluctuate but slowly rose or fell depending on changes in the room temperature.

Boiling Apparatus. Two types of boiling apparatus shown in Fig. 2 were used, one corresponding to the minimum and one to the maximum internal diameter recommended in the international standard procedure.

The smaller boiling tube, which is used in our standard procedure, was made of pyrex glass, 4.2 cm. (ca. 1 5/8 in.) internal diameter,

[5] J. A. Beattie, Proc. Am. Acad. Arts and Sci., **69,** 389 (1934).

4.6. cm. (ca. 1 13/16 in.) outside diameter and 100 cm. long over all. It had a side arm near the top which was connected to the manostat by glass or heavy rubber tubing. The platinum resistance thermometer to be calibrated was slipped into a protection tube and inserted through a rubber stopper at the top.

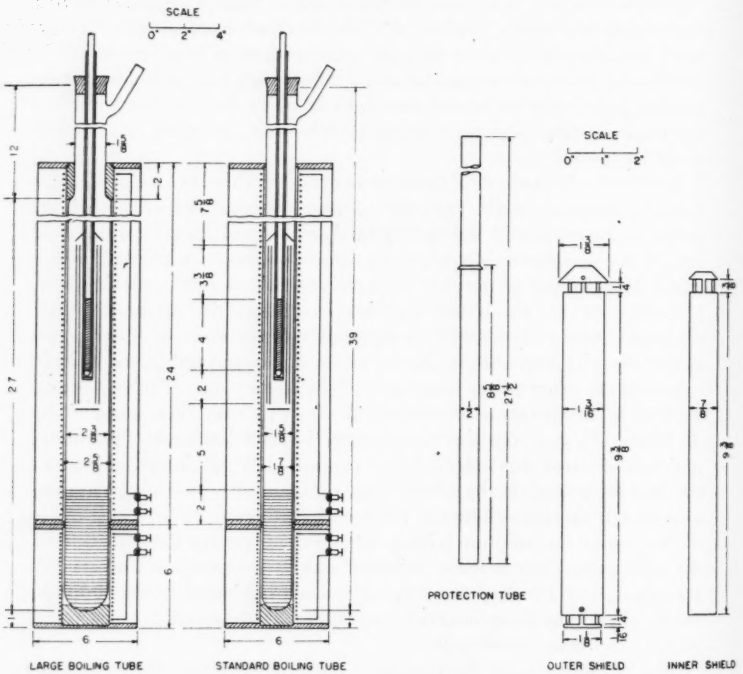

FIGURE 2. Details of the boiling apparatus. Dimensions are in inches.

The sulphur was heated to boiling by means of an electric heating unit 6 in. long. The outside of the furnace was made from a piece of seamless steel tubing 6 in. outside diameter and 1/8 in. wall thickness, closed at the top and bottom with ¼ in. thick transite plugs. The heating element was number 21 Chromel "A" asbestos-covered wire of 10 ohms resistance wound on seamless steel tubing 2 in. outside diameter and 1/16 in. wall thickness (4.75 cm. bore) and insulated

from it by means of mica. The annular space was filled with mineral wool.

The insulating unit was 24 in. long, and constructed in the same manner as the heating unit except that the heating element was of 30 ohms resistance and was wound on an asbestos tube 1 7/8 in. (4.75 cm.) internal diameter made by wrapping asbestos paper thoroughly wet with water glass around an oiled steel tube of the proper external diameter. The energy input necessary to heat the insulating unit to any desired temperature was determined experimentally.

The larger boiling tube was 6.0 cm. (ca. 2 3/8 in.) internal diameter. We could not obtain a stable sulphur-vapor helium boundary in a tube as wide as this as indicated by a pressure oscillation. Hence the upper 12 in. was made of 4.2 cm. internal diameter tubing, The heating and insulating units were similar in construction to those used for the smaller boiling tube.

Protection Tube. The windings and leads of the platinum resistance thermometer were encased in a pyrex glass tube. For the determination of the sulphur point the thermometers were slipped into an aluminum-manganese alloy (designated 3S by the Aluminum Company of America) protection tube ½ in. outside diameter and 0.020 in. wall thickness. The bottom was welded vacuum-tight. The radiation shields were hung from a small truncated aluminum cone which fitted tightly around the tube and was forced over a knurled place 8 5/8 in. from the bottom.

The effect of using protection tubes of pure aluminum (0.035 in. wall thickness), nickel (0.020 in. wall thickness), and pyrex glass (0.05 in. wall thickness) was studied.

Shields. The shields used are shown in Fig. 2.

The outer shield was made of aluminum 0.020 in. wall thickness, blackened with India drawing ink on the inner surface, and was 1 3/16 in. (30.2 mm.) outside diameter and 9 3/8 in. long. It was riveted to and supported by an umbrella 1 3/8 in. diameter at its largest part, ½ in. at its smallest part spun from pure aluminum. The umbrella was a tight fit on the protection tube and extended about 3/32 in. beyond the shield, thus preventing liquid sulphur from draining down onto the shield.

An aluminum radiation disk (blackened on its upper side) 1/16 in. thick and 1 1/8 in. diameter could be attached to the bottom of the shield by three small screws which also served to keep the innershield concentric with the outer. The purpose of the disk was to prevent the protection tube from being over-heated by radiation or splashing

from the superheated liquid sulphur. The umbrella and the radiation disk were each spaced ¼ in. from the end of the radiation shield,

The inner radiation shield, also blackened on its inner surface, was made from aluminum tubing 0.020 in. wall thickness, and was 7/8 in. (22.2 mm.) outside diameter and 9 3/8 in. long. A conical cap by which it was supported was spun on the upper end. There was an opening of 3/8 in. between the cap and the shield.

The two shields and the radiation disk were used in our standard procedure. The effect of omitting the inner shield and the radiation disk was studied.

Sulphur. The work of Mueller and Burgess[6] indicates that 0.1% of arsenic may raise the sulphur point by about 0.01° C., and 0.1% of selenium, by about 0.05° C.

We used two grades of sulphur. The first was precipitated sulphur U. S. P. which was not analyzed but which gave almost the same sulphur point as the second sample. For the greater part of the work and for the determination of the effect of pressure on the sulphur point, there was used sublimed sulphur U. S. P. from Merck and Company, Rahway, New Jersey, which was refined from crude sulphur mined in Texas. It was analyzed for selenium and arsenic by Dr. G. G. Marvin.[7] The results are given in Table I. The impurities should affect the sulphur point by less than 0.001° C. No correction was applied for this effect.

TABLE I

ANALYSIS OF THE SULPHUR

Selenium	Less than 0.001%
Arsenic	Less than 0.002%, but greater than 0.001%
Non-volatile matter	Less than 0.01%

3. EXPERIMENTAL PROCEDURE

The apparatus used in our standard procedure is shown in Fig. 2. Sufficient sublimed sulphur was put into the boiling tube to bring the level of the liquid to at least 2 in. above the top of the heating unit. Since no sulphur was lost by distillation or oxidation, one filling sufficed for many calibrations. The protection tube carrying the radiation shields was carefully centered in the boiling tube and was not thereafter removed. The boiling tube was placed in the furnace and the side arm connected to the manostat which was kept filled with

[6] Mueller and Burgess, loc. cit.

[7] G. G. Marvin and W. C. Schumb., Anal. Ed., Ind. Eng. Chem., **7**, 423 (1935).

helium. Heat was applied and when the sulphur was melted, the boiling tube was evacuated and filled with dry helium. The platinum resistance thermometer to be calibrated was inserted into the protection tube.

The insulating unit was heated to 400° C. and air from an electric fan blown on the exposed portion of the boiling tube. The current in the heating unit was adjusted until the condensation line of sulphur was 2 cm. above the top of the insulating unit.

The barometer was filled with dry helium and connected to the manostat, and the pressure in the manostat was adjusted to the desired value. For calibrating a resistance thermometer we adjusted the pressure to within 1 mm. of 760 mm.

After the temperature of the thermometer had remained constant to 0.001° C. for ten minutes the calibration (or determination) was started. The resistance of the platinum thermometer was measured with the commutator set in the normal (N) and reverse (R) position with the battery current passing in the direct and then in the reverse direction. The average of the four readings gave the resistance of the thermometer. The cross-hair of the telescope was set two times on the crown of the upper mercury surface and the average reading M_u of the micrometer head noted: the operation was repeated with the lower telescope and the average reading M_l obtained. The bar and telescopes were then rotated as a unit to the scale and the cross-hair of the upper telescope brought into coincidence with the nearest scale division D_u, and the cross-hair of the lower telescope to the nearest scale division D_l. The new readings (average of two values) of the micrometer heads, S_u and S_l, for, respectively, the upper and lower telescopes were noted. The uncorrected difference $L_1 - L_2$ in elevation between the mercury surfaces is

$$L_1 - L_2 = D_u - D_l + M_u - M_l - S_u + S_l. \tag{9}$$

For a calibration (or determination) this process was repeated five times and the average of the five readings of resistance and mercury height used in the subsequent computations.

When the boiling tube was removed from the heater it was placed at an angle of 10° to the horizontal and the sulphur allowed to solidify while the tube was in this position. When the tube was to be heated again, it was placed directly in the furnace without preliminary heating.

After the completion of each determination the ice point of the thermometer was measured. A Dewar tube, 3 in. in diameter and 24

in. long, encased in a wooden box was filled with finely shaven ice and wet with distilled water which had been cooled in an ice chest and saturated with laboratory air. The bare thermometer was inserted along the axis of the tube to within 2 in. of the bottom and the mixture was stirred by means of a stainless steel rod with a hoop at the bottom. The ice point was checked after the water had been drained off through a nickel wire screen, and fresh cooled water added.

4. Corrections

Resistance Readings. The resistance bridge has been calibrated periodically since 1930, the corrections being determined to approximately 3×10^{-6} ohms in terms of a 100 ohm coil. The corrections vary in a fairly regular manner with time. The corrections used in the present investigation were determined by linear interpolation with time between calibrations made before and after the work. The ratio arms of the bridge were balanced at each calibration and the setting not changed between calibrations.

Each morning the "zero balance" of the bridge was determined[8] and this value, which varied slowly with time from 0.00005 to 0.00008 ohms, subtracted from all resistance readings for the day. At the same time the ratio coils were interchanged and an estimate of the ratio of their resistances obtained. This ratio varied slowly with time from 1 to 1.000003. As shown in the Appendix the error due to the unbalance of the ratio coils can be reduced to 0.0001° C. in the most unfavorable case by determining an ice point of the thermometer on each day and using this resistance for all computations of temperatures measured on that day.

Ice Points. The ice point $t°$ C. is given by the relation

$$t = -0.0098\frac{p - 760}{760} - 0.0075\frac{H}{13.6 \times 760} \qquad (10)$$

where p is the barometric pressure in mm. at which the water was saturated with air and H is the level of water in mm. above the mid-point of the thermometer coil (500 mm. in our work). For thermometers of about 25 ohms resistance this correction can be applied by subtracting $0.1t$ ohms from the observed resistance.

Pressure. In order to obtain the pressure at the mid-point of the platinum resistance thermometer winding several corrections must be applied to the observed barometric height. These corrections are conveniently grouped under three headings.

[8] See E. F. Mueller, Bull. Bur. Standards, **13,** 547 (1916–1917).

Scale Corrections. The observed readings were corrected for

(1) the ruling error of the scale
(2) the thermal expansion of the scale
(3) the extension of the scale due to its weight

by means of the relation

$$p'' = [L_1 - L_2 + \delta_1 - \delta_2][1 + \alpha_i (t - 20)] + \frac{\rho_i g}{20 E_i}[L_1^2 - L_2^2]; \quad (11)$$

where

p'' = pressure in mm. corrected for scale corrections
L_1 = scale reading in mm. corresponding to upper mercury surface
L_2 = scale reading in mm. corresponding to lower mercury surface
δ_1 = scale calibration correction in mm. for L_1
δ_2 = scale calibration correction in mm. for L_2
$\alpha_i = 1.5 \times 10^{-6} C^{0-1}$ = coefficient of thermal expansion of invar at room temperature.[9]
t = scale temperature (°C.)
$\rho_i = 8$ gms./cm.^{3} = density of invar
$g = 980.400$ dynes/gms. = gravity at the laboratory
$E_i = 1.5 \times 10^{12}$ dynes/cm.^{2} = Young's modulus for invar.[10]

For invar Eq. (11) becomes

$$p'' \text{ (mm.)} = L_1 - L_2 + \delta_1 - \delta_2 + 1.5 \times 10^{-6}(t - 20)(L_1 - L_2) + 2.61 \times 10^{-10}(L_1^2 - L_2^2) \quad (12)$$

when L_1 and L_2 are expressed in millimeters. In the pressure range from 660 to 860 mm. and when $L_2 = 150$ mm. at 760 mm., the last term of Eq. (11) is 0.0002 ± 0.00004 mm. Thus for our work

$$p'' \text{ (mm.)} = L_1 - L_2 + \delta_1 - \delta_2 + 1.5 \times 10^{-6}(t - 20)(L_1 - L_2) + 0.0002 \quad (13)$$

Mercury Corrections. The pressure p'' was then corrected for:

(1) The difference in the capillary depression of mercury in the upper and lower barometer tube
(2) the thermal expansion of mercury
(3) the compressibility of mercury
(4) the effect of gravity

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[9] Determined at U. S. Bureau of Standards, Certificate TW1 – 54661.
[10] International Critical Tables, Vol. II, p. 481 (1927).

by the relation

$$p' \text{ (mm.)} = p'' \frac{V_s}{V_{p,t}} \frac{g_l}{g_s} - 0.0013; \tag{14}$$

where

p' = pressure in mm. corrected for scale and mercury corrections

V_s = 13.5951 gms./cm.^{3} = average density of a column of mercury 760 mm. high in vacuo at 0°C. and standard gravity.

$$V_{p,t} = V_s[1 + f(t)]\left[1 - \frac{\beta}{2}\left(\frac{p'}{760} - 1\right)\right]$$

$10^6 f(t) = 181.456t + 9.205 \times 10^{-3}t^2 + 6.608 \times 10^{-6}t^3 + 67.320 \times 10^{-9}t^4$ = function for the effect of temperature on the specific volume of mercury at 1 atm. (t = °C.).[11]

$\beta = 4 \times 10^{-6}$ atm.$^{-1}$ = compressibility of mercury

g_l = 980.400 dynes/gm. = value of gravity at the laboratory

g_s = 980.665 dynes/gm. = standard gravity

0.0013 = capillary depression of mercury correction.[12]

Substitution of the above values into Eq. (14) gives

$$p' \text{ (mm.)} = p'' F + \Delta - 0.0013 \tag{15}$$

The values of $F = 0.9997\ 2978/[1 + f(t)]$ are recorded in tables for 0.1 intervals in t. The compressibility correction Δ is -2×10^{-4} mm. for a column of mercury 660 mm. high and $+2 \times 10^{-4}$ mm. for a column 860 mm. high, and is of course 0 at 760 mm.

Static Head Corrections. The pressure p' was then corrected for

(1) the static head of sulphur vapor

(2) the static head of the permanent gas used to transmit the pressure to the barometer by the relation:

$$p \text{ (mm.)} = p' + l_1 r_1 + l_2 r_2 \tag{16}$$

where

p = the true pressure in standard mm. of mercury at the mid-point of the platinum resistance thermometer winding

[11] International Critical Tables, Vol. II, p. 457 (1927).

[12] The bore of the barometer tubes was 32 mm. The average height of the meniscus in the upper tube was 0.75 ± 0.05 mm., and that in the lower tube, 1.75 ± 0.05 mm. The correction on the measured height, due to capillary depression, as computed from the Lohnstein formula (μ = 0.8, a = 2.670) is + 0.0012 ± 0.00008 mm. for the upper meniscus and − 0.0025 ± 0.00005 mm. for the lower. The net correction is thus − 0.0013 ± 0.0001 mm.

l_1 = the distance in mm. from the mid-point of the thermometer winding to the condensation line of sulphur, considered positive in the upward direction

l_2 = the distance in mm. from the condensation line of sulphur to the lower mercury meniscus in the barometer, considered positive in the upward direction

r_1 = ratio of density of saturated sulphur vapor at the pressure p (ca. p') to the density of mercury. See Table II.

TABLE II

VALUES OF THE RATIO (r_1) OF THE DENSITY OF SATURATED SULPHUR VAPOR AT THE SATURATION PRESSURES p TO THE DENSITY OF MERCURY

$$r_1 = \frac{219.5}{82.06 \times 760 \times 13.5951} \frac{p}{(t + 273.1)}$$

$$t = 444.6 + 9.08 \frac{p - 760}{100} - 0.48 \left(\frac{p - 760}{100}\right)^2 + 0.04 \left(\frac{p - 760}{100}\right)^3$$

p (mm.)	$r_1 \times 10^6$	p (mm.)	$r_1 \times 10^6$	p (mm.)	$r_1 \times 10^6$
660	241	730	264	800	287
670	245	740	268	810	290
680	248	750	271	820	294
690	251	760	274	830	297
700	254	770	277	840	300
710	258	780	281	850	303
720	261	790	284	860	307

See Appendix for the value of the molecular weight of saturated sulphur vapor.

r_2 = ratio of density of nitrogen (or helium) at the pressure p (ca. p') and at room temperature to the density of mercury. See Table III.

The final corrected pressure is given by the relation

$$p \text{ (mm.)} = [L_1 - L_2 + \delta_1 - \delta_2 + 1.5 \times 10^{-6}(t - 20)(L_1 - L_2)]F - 0.001 + l_1 r_1 + l_2 r_2. \quad (17)$$

The uncertainty in using this approximate equation does not exceed 0.001 mm. which corresponds to an error of 0.0001° C. in the sulphur point.

TABLE III

VALUES OF THE RATIO (r_2) OF THE DENSITY OF NITROGEN AND HELIUM AT THE PRESSURE p AND AT ROOM TEMPERATURES TO THE DENSITY OF MERCURY

Nitrogen

$$r_2 = \frac{28.016\,p}{82.06 \times 760 \times 13.5951 \times 298.1}$$

p (mm.)	660	710	760	810	860
$r_2 \times 10^6$	73	79	84	90	95

Helium

$$r_2 = \frac{4.002\,p}{82.06 \times 760 \times 13.5951 \times 298.1}$$

p (mm.)	660	710	760	810	860
$r_2 \times 10^6$	10	11	12	13	14

The error in using the above values for room temperatures of from 20° to 30° C. is less than 2×10^{-6} in the value of r_2.

5. Effect of Variation of Conditions on the Indicated Temperature

In Table IV are given the results of a study of the effect of varying one condition at a time on the temperature of the sulphur point. Under each heading all conditions are the same as in the standard procedure given in Section 3, except those specifically mentioned as being varied. Each entry represents a single determination. In this earlier work the method of lighting the mercury menisci was not as satisfactory as that described in Section 2, and uncertainties of 0.002 to 0.003° C. existed.

The pressure for each determination was adjusted until it was well within 1 mm. of 760 mm. In order that all measurements be on a comparable basis the values were reduced to the normal sulphur point. The measured resistance R_p of the thermometer at the corrected pressure p mm. was reduced to the resistance R_{760} which would have been read had the pressure been exactly 760 mm. By the relation (see Appendix)

$$R_{760} = R_p - 3.140 \times 10^{-4} R_0 (p - 760), \qquad (18)$$

where R_0 is the ice point resistance of the thermometer. The platinum temperature t_{pt} was then computed from the relation

$$t_{pt} = \frac{R_{760} - R_0}{\alpha R_0}, \tag{19}$$

and the deviation Δt_{pt} of the platinum temperature from the standard procedure converted into $\Delta t°$ C. Int. by the relation

$$\Delta t° \text{ C. Int.} = \frac{\Delta t_{pt}}{0.8823}. \tag{20}$$

Since the pressure was never as much as 1 mm. away from 760 mm. the error introduced by these approximations does not exceed 0.0001°C.

TABLE IV

EFFECT OF VARIATION OF CONDITIONS ON THE INDICATED TEMPERATURE

Condition Varied	Effect $10^3\Delta t°$ C.(Int.)	
A. Sulphur		
Sublimed (two determinations)	± 0.0 (s)	
Precipitated (two determinations)	+ 2.2	
B. Height of condensation line of sulphur above top of insulating unit		
1 cm.	± 0.0	
2 cm.	± 0.0 (s)	
3 cm.	+ 0.7	
C. Distance from top of insulating unit to mid-point of thermometer coil	Radiation Shields	
	Standard Shielding	Outer Shield Only
18 cm.	− 5.2	− 6.1
23 cm.	− 1.9	− 1.5
28 cm.	± 0.0	± 0.0
33 cm.	± 0.0 (s)	+ 0.7
38 cm.	± 0.0	—
D. Protection Tube		
Aluminum Alloy (0.020 inch wall)	± 0.0 (s)	
Pure Aluminum (0.035 inch wall)	± 0.0	
Nickel (0.020 inch wall)	+ 12.4	
Glass (0.050 inch wall)	− 15.0	
Glass filled with solder	+ 1.2	
E. Temperature of insulating unit		
30° C.	+ 0.5	
250	+ 3.2	
350	+ 2.9	
400	± 0.0 (s)	
420	+ 1.3	

TABLE IV—*Continued*

F. Method of shielding

Protection Tube	Radiation Shields	Temp. of Insulating Unit 30° C.	400° C.
Aluminum alloy	Both shields with disk....	+ 0.6	± 0.0 (s)
Aluminum alloy	Both shields without disk.	+ 2.0	+ 2.6
Aluminum alloy	Outer shield only.....	+ 0.6	+ 0.8
Glass	Outer shield only.....	− 14.4	± 0.0

G. Boiling tubes	Temp. of Insulating Unit 30° C.	400° C.
Small boiling tube (4.2 cm.).....	+ 0.6	± 0.0 (s)
Large boiling tube (6.0 cm.).....	− 0.1	+ 0.7

(s) = standard procedure.

In the above table conditions not mentioned are standard. Standard procedure: sulphur, sublimed; height of condensation line above top of insulating unit, 2 cm.; distance from top of insulating unit to mid-point of coil, 33 cm.; protection tube, aluminum-alloy; temperature of insulating unit, 400° C.; method of shielding, two shields and disk; boiling tube, small (4.2 cm. internal diameter).

The following results may be mentioned:

A. The precipitated sulphur, which was not analyzed, gave a slightly higher sulphur point. The difference is hardly significant.

B. A change in the rate of heating sufficient to cause a variation of from 1 to 3 cm. in the height of the condensation line sulphur above the top of the insulating unit produces no effect on the sulphur point; when the height is increased to 7 cm. the temperature becomes unsteady.

C. Whether two radiation shields and disk or a single radiation shield without disk are used, the reading of the thermometer is practically independent of the distance of the mid-point of the coil below the top of the insulating unit provided the distance is over 25 cm.

D. The greatest effect was obtained when different protection tubes were used. A nickel tube gives high results due, no doubt, to the heat of reaction of sulphur with nickel, which is quite rapid for a fresh nickel surface. The use of a glass protection tube which is a quite common procedure leads to low results as compared to metal. When the glass tube is filled with solder or when the insulating unit is heated to 400° C. (See F) the temperature becomes normal.

E. The "temperature of the insulating unit" given in the table are

those read on a thermometer placed in the center of the unit, both ends being plugged with asbestos paper. The current determined in this manner was run through the unit when used in a sulphur point determination, the current input into the heater being adjusted so that the condensation line of sulphur is in the standard position. The high results at 250 and 350° C. are difficult to explain on any other basis than experimental error, since no real effect existed at 400 and 420° C.

F. The slightly increased temperature when two shields are used suggests that one shield alone is not quite sufficient. However, the addition of the disk reduced the temperature to that obtained with only one shield.

G. The large and small boiling tube give the same temperature for the sulphur point. It should be noted that we could not obtain a stable sulphur-vapor-helium boundary in a 6 cm. tube.

Table IV shows that rather wide variations from our standard procedure are without an effect greater than 0.002° C. on the sulphur point.

6. The Effect of Pressure on the Sulphur Point

Four runs each consisting of from 8 to 10 determinations and each covering approximately the pressure range 660 to 860 mm. were made to investigate the effect of pressure on the sulphur point. Two platinum resistance thermometers and two barometers were used. The standard procedure was followed. The pressures and resistances were corrected by the method given in Section 4. Each run was completed on a single day and the ice point of the thermometer determined immediately after the run.

The value of α for each thermometer was determined from the data resulting from a study of the effect of pressure on the steam point. The uncertainty in the values of α is approximately 0.000 000 025, which introduces an uncertainty of less than 0.0001° C. in the temperature at 660 or 880 mm. relative to the temperature at 760 mm. (See the Appendix.)

In order that each run pass through 444.6° C. at 760 mm., a value of δ was computed from the four or five determinations nearest one atmosphere pressure (determination No. 62 was omitted because of its large deviation). Several approximations were required to make all of the values consistent to 0.0001° C. For the first approximation the temperatures used for computing a provisional value of δ were calculated from the international equation, Eq. (1), and the observed pressures p. From the resistances R_t and the values of R_0, α, and this

TABLE V

THE EFFECT OF PRESSURE ON THE SULPHUR POINT

$$t_{calc} \equiv t_p = 444.6 + 0.0908028\,(p-760) - 0.000\,047573\,(p-760)^2 + 0.000\,000\,04361\,(p-760)^3$$

$$t_{obs} = \frac{R_t - R_o}{R_o\alpha} + \delta\left(\frac{t_{obs}}{100}\right)\left(\frac{t_{obs}}{100} - 1\right)$$

Run No.	Determination No.	Barometer	Pressure Standard mm.	Thermometer No.	R_t	R_0, α, δ	t_{obs}, °C. Int.	$(t_{obs}-t_{calc})\times 10^3$ °C. Int.	R_0, α, δ	t_{obs}, °C. Int.	$(t_{obs}-t_{calc})\times 10^3$ °C. Int.
						Different δ used for each run			Average δ used for each thermometer		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1	57	Right	829.848	107	67.11629	25.09081	450.7208	−4.4	25.09081	450.7226	−2.6
	58		811.457		66.98024	0.003921378	449.1506	−1.8	0.003921378	449.1524	0.0
	59		792.804		66.83986	1.49241	447.5313	+2.3	1.49251	447.5331	+4.1
	60		774.425		66.69832		445.8996	−0.5		445.9013	+1.2
	61		751.795		66.52057		443.8516	−0.1		443.8533	+1.6
	62		733.684		66.37558		442.1822	+5.5		442.1839	+7.2
	63		711.878		66.19599		440.1156	+0.2		440.1173	+1.9
	64		692.877		66.03648		438.2813	+3.8		438.2830	+5.5
	65		672.450		65.86030		436.2567	+0.4		436.2583	+2.0
2	65′	Right	663.230	308	67.57782	25.77501	435.3314	+3.4	25.77501	435.3315	+3.5
	66		682.004		67.74559	0.003921693	437.2073	−0.3	0.003921693	437.2075	−0.1
	67		702.796		67.92741	1.49175	439.2417	−0.2	1.49176	439.2419	0.0
	68		721.924		68.09080		441.0711	−0.1		441.0712	0.0
	69		741.724		68.25621		442.9242	−0.1		442 9244	+0.1
	70		759.576		68.40229		444.5617	+0.2		444.5619	+0.4
	71		780.574		68.57062		446.4498	+1.4		446.4500	+1.6
	72		798.915		68.71433		448.0627	−1.4		448.0629	−1.2
	73		821.348		68.88688		450.0004	−1.2		450.0006	−1.0
	74		839.182		69.02148		451.5128	−0.5		451.5130	−0.3

TABLE V—*Continued*

THE EFFECT OF PRESSURE ON THE SULPHUR POINT

Run No.	Determination No.	Barometer	Pressure Standard mm.	Thermometer No.	R_t	R_0, α, δ	t_{obs}, °C. Int.	$(t_{obs}-t_{calc})\times 10^3$ °C. Int.	R_0, α, δ	t_{obs}, °C. Int.	$(t_{obs}-t_{calc})\times 10^3$ °C. Int.
						Different δ used for each run			Average δ used for each thermometer		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
3	75	Right	849.262	308	69.09710	25.77511	452.3604	+3.2	25.77511	452.3600	+2.8
	76		830.191		68.95431	0.003921693	450.7555	+1.3	0.003921693	450.7552	+1.0
	77		807.021		68.77751	1.49178	448.7696	+0.6	1.49176	448.7692	+0.2
	78		790.933		68.65255		447.3667	+2.1		447.3664	+1.8
	79		769.127		68.47953		445.4255	+0.7		445.4251	+0.3
	80		750.718		68.33029		443.7521	−0.9		443.7517	−1.3
	81		728.890		68.14952		441.7263	−1.5		441.7260	−1.8
	82		708.677		67.97807		439.8063	−2.2		439.8060	−2.5
	83		686.635		67.78630		437.6603	−4.7		437.6599	−5.1
	84		668.741		67.62713		435.8802	−3.9		435.8799	−4.2
4	85	Left	682.284	107	65.94550	25.09085	437.2379	+2.5	25.09085	437.2361	+0.7
	86		704.873		66.13720	0.003921378	439.4417	−0.7	0.003921378	439.4399	−2.5
	87		726.718		66.31810	1.49262	441.5229	−0.7	1.49251	441.5211	−2.5
	88		746.436		66.47765		443.3597	+0.2		443.3578	−1.7
	89		763.389		66.61195		444.9067	−0.5		444.9048	−2.4
	90		784.385		66.77513		446.7874	+0.8		446.7855	−1.1
	91		805.038		66.93220		448.5989	+1.8		448.5969	−0.2
	92		825.358		67.08325		450.3420	−1.6		450.3400	−3.6
							Average Deviation 1.6			Average Deviation 1.9	

TABLE VI

Computation of δ

$$t_p = 444.6 + 0.0908028\,(p - 760) - 0.000\,047573\,(p - 760)^2 + 0.000\,000\,04361\,(p - 760)^3$$

$$\delta\left(\frac{t_p}{100}\right)\left(\frac{t_p}{100} - 1\right) = t_p - \frac{R_t - R_0}{R_0\alpha}$$

Thermometer No.	107	308
α	0.003921378	0.003921693

Run No.	Determination No.	Thermometer No.	t_p	$\frac{R_t - R_0}{R_0\alpha}$	δ
1	58	107	449.1524	425.74648	1.492509
	59		447.5290	424.31971	1.492278
	60		445.9001	422.88116	1.492441
	61		443.8517	421.07458	1.492415
	63		440.1154	417.77569	1.492398
			δ for Run No. 1		1.49241
2	68	308	441.0712	418.62968	1.491758
	69		442.9243	420.26608	1.491757
	70		444.5615	421.71125	1.491737
	71		446.4484	423.37654	1.491670
	72		448.0641	424.79826	1.491830
			δ for Run No. 2		1.49175
3	78	308	447.3646	424.18443	1.491659
	79		445.4248	422.47276	1.491741
	80		443.7530	420.99633	1.491835
	81		441.7278	419.20798	1.491866
			δ for Run No. 3		1.49178
4	87	107	441.5236	419.01569	1.492659
	88		443.3595	420.63729	1.492607
	89		444.9072	422.00225	1.492649
	90		446.7866	423.66074	1.492573
			δ for Run No. 4		1.49262
			δ for Thermometer No. 107		1.49251
			δ for Thermometer No. 308		1.49176

provisional value of δ, we computed the observed temperatures for all of the determinations and the constants of a cubic equation

$$(t_{obs} - 444.6) = A(p - 760) + B(p - 760)^2 + C(p - 760)^3 \quad (21)$$

by the method of least squares. From the temperatures computed from this equation new values of δ were determined and the computation carried through a second time to give the final values of A, B, and

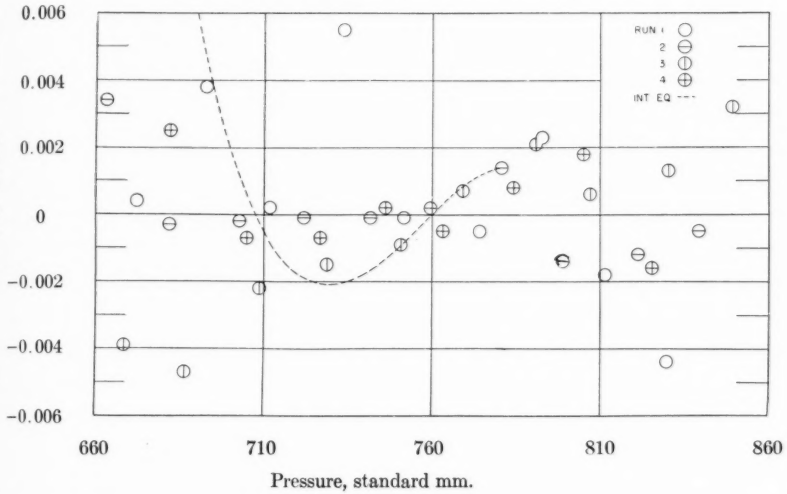

FIGURE 3. Plot of the observed temperatures minus the temperatures calculated by Equation (22) against the pressures [column (9) against column (4) of Table V]. For computing the observed temperatures a different value of δ was used for each run.

C. Use of temperatures computed from this final equation did not change the values of δ to the number of significant figures used. The data for the calculation of the final values of δ are given in Table VI.

The final equation for the effect of pressure on the sulphur point is

$$t_p = 444.6 + 0.0908028(p - 760) - 0.000\,047573(p - 760)^2 + 0.000\,000\,04361(p - 760)^3 \quad (22)$$

where p is in standard mm. of mercury and t_p is the corresponding saturation temperature on the *international temperature scale*. The

data are given in Table V. That t_p is not on the absolute temperature scale is due to two causes: (1) the values of the constants of the above equation depend on the value 444.6 for the normal sulphur point, and this value is about 0.1° C. too low; (2) a cubic equation, at least, is required to express the resistance of a platinum thermometer in terms

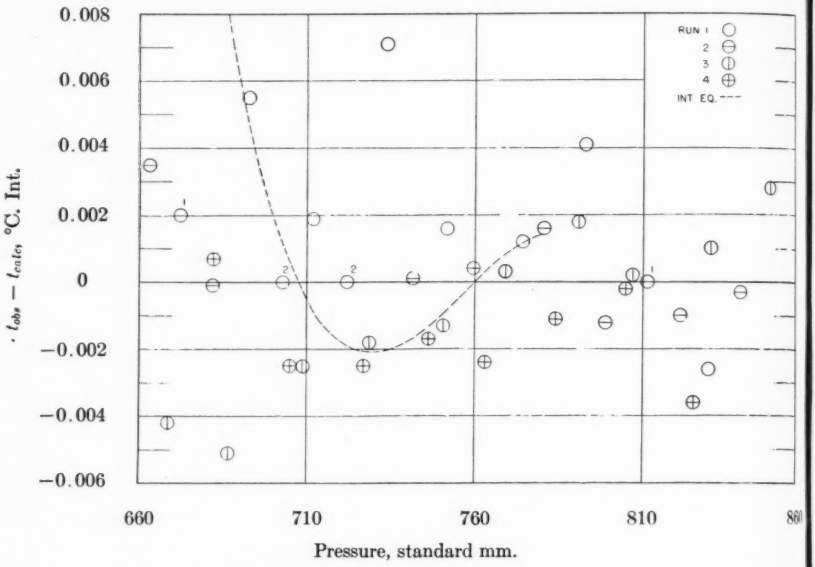

FIGURE 4. Plot of the observed temperatures minus the temperatures calculated by Equation (22) against the pressures [column (12) against column (4) of Table V]. For computing the observed temperatures a different value of δ was used for each thermometer.

of absolute temperatures in the range 0° to 444.6° C. with an accuracy (in terms of temperature) of 0.01° C. or better.

In columns 8 and 9 of Table V are given the temperatures t_{obs} computed from the observed resistances R_t, and the deviations of the temperatures calculated by Eq. (22), from the observed values. The thermometer constants used are given in column 7. The deviations are plotted in Fig. 3; the average deviation is $\pm$ 0.0016° C. In the last three columns (10, 11, 12) of Table V are given the computations based on one value of δ for each thermometer, instead of a different

value of δ for each run. The deviations of the calculated from these observed values are plotted in Fig. 4; they are of course somewhat larger than those resulting when different values of δ are used for each run, the average being $\pm$ 0.0019° C.

The dotted lines of Figs. 4 and 5 represent the temperatures calculated from the international equation, Eq. (1), minus those calculated from our equation, Eq. (22). Our equation gives a temperature differing from the international equation by .012° C. at 680 and .001° C. at 780 mm.

We wish to thank the National Research Council for a grant from the Grants-in-Aid, and the American Academy of Arts and Sciences for a grant from the Permanent Science Fund which made possible the latter portion of this work.

7. Summary

An apparatus for controlling and reproducing the sulphur point to a precision of about 0.002° C. is described. The results of a comprehensive study of the variables affecting the reproducibility of the sulphur point are given.

In the range 660 to 860 mm. the temperature t_p °C. (Int.) of equilibrium between liquid sulphur and its vapor at a pressure p standard mm. of mercury is given by the relation

$$t_p = 444.6 + 0.0908028(p - 760) - 0.000\,047573(p - 760)^2 + 0.000\,000\,04361(p - 760).^3$$

The average deviation of 37 determinations from the equation is less than $\pm$ 0.002° C.

8. Appendix

Correction for Lack of Balance in the Ratio Coils and in the X and R Arms of the Resistance Bridge. In the Mueller Wheatstone bridge the resistances in the X and R arms are not zero when all dials are set on zero. A difference in the resistances of these two arms (including the lead wires to the commutator) introduces an error in the measured temperature as computed from the Callendar equation. The "zero balance" described by Mueller[13] eliminates this effect. There is also an error due to the unbalance of the ratio coils. If the ratio of the resistances of the ratio coils does not exceed 1.000 003, no error greater than 0.0001° C. is introduced at the sulphur point when the ice point resistance of the thermometer is taken each day and used for the computation of temperatures measured on that day.

[13] E. F. Mueller, loc. cit.

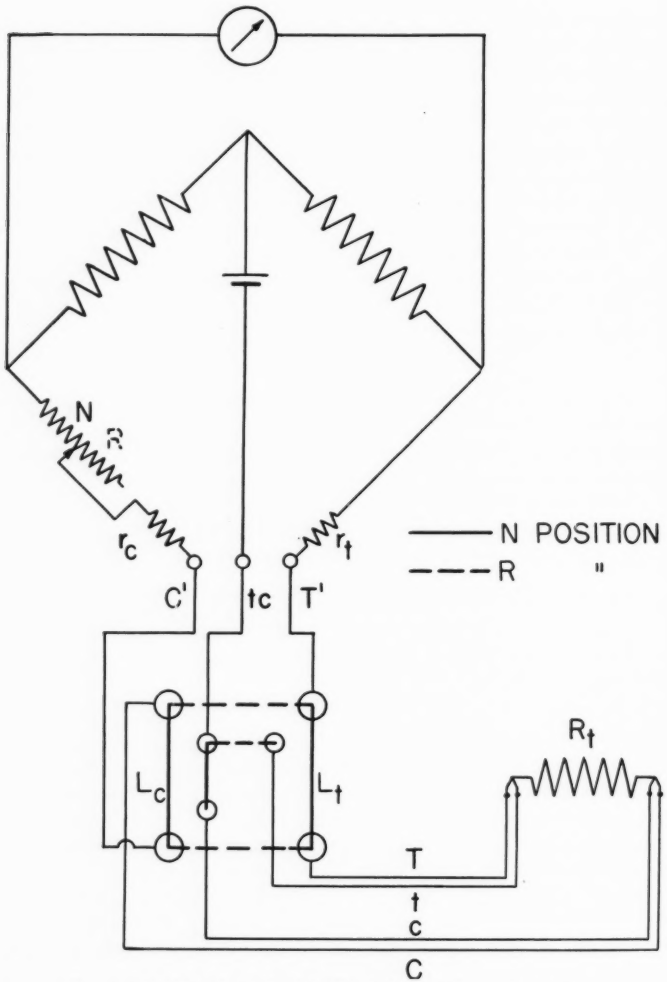

FIGURE 5. Sketch of the Mueller bridge and commutator.

In Fig. 5 let:

R_t = true resistance of the platinum thermometer at $t°$.
N = bridge reading for balance with commutator in N position.
R = bridge reading for balance with commutator in R position.
$r_c \cong r_t \cong 1.5$ ohms = resistances remaining in R and X arms of bridge, respectively, when all dials are set on zero.
$L_c \cong L_t \cong 0.000\,01$ ohm = resistances of commutator links.
$C' \cong T' \cong 0.0002$ ohm = resistances of leads from bridge to commutator.
$C \cong T \cong 0.75$ ohm when thermometer is at the ice point to 1 ohm when at the sulphur point = resistances of leads from commutator to Y in thermometer.
$1 + \varepsilon$ = ratio of resistances of ratio arms, where ε varied from 0 to 0.000 003.

When the commutator is in the N position

$$\frac{r_t + T' + L_t + T + R_t}{N + r_c + C' + L_c + C} = 1 + \varepsilon; \tag{23}$$

when in the R position

$$\frac{r_t + T' + L_c + C + R_t}{R + r_c + C' + L_t + T} = 1 + \varepsilon; \tag{24}$$

whence

$$R_t = \left(\frac{N + R}{2} + \Delta\right)(1 + \varepsilon) + \frac{\varepsilon \Lambda_t}{2} \tag{25}$$

where

$$\Delta = (r_c + C') - (r_t + T') = \text{"zero balance" reading} \tag{26}$$

$$\Lambda_t = 2r_t + 2T' + C + T + L_c + L_t \tag{27}$$

$\cong 4.5$ ohms when thermometer is at the ice point to 5.0 ohms when at the sulphur point.

$\varepsilon\Lambda_t/2 = 0$ to a maximum value of 0.000 008.

At the beginning of each day we determined Δ and ε by short-circuiting the T' and C' poles of the commutator by means of a link, the middle of which was connected to the $t'c'$ pole, and measuring the resistance necessary for balance (from the galvanometer swing) when the ratio coils were in their normal position and when interchanged.

Let $L \backsimeq 0.000\,01$ ohm = resistance of short-circuiting link.
R_o = bridge reading for balance when all dials are set on zero.
R_r = bridge reading for balance when 1.0 and 0.1 dials are each set on R (ratio coils interchanged).
$R_o \backsimeq R_r = 0.000\,05$ to $0.000\,08$ ohm.

When the ratio coils were in their normal position,

$$\frac{r_t + T' + \tfrac{1}{2}L}{R_o + r_c + C' + \tfrac{1}{2}L} = 1 + \varepsilon; \tag{28}$$

when interchanged

$$\frac{r_t + T' + \tfrac{1}{2}L}{R_r + r_c + C' + \tfrac{1}{2}L} = 1 - \varepsilon; \tag{29}$$

whence

$$\Delta = -\frac{R_o + R_r}{2} \tag{30}$$

$$\varepsilon = \frac{R_r - R_o}{-2\Delta + 2r_c + 2C' + L} \backsimeq \frac{R_r - R_o}{3} \tag{31}$$

The Δ correction, which varied slowly with time from $0.000\,05$ to $0.000\,08$ ohm, was added to all values of $(N + R)/2$ for that day, and the term $(N + R)/2 + \Delta\,[= (R_t - \varepsilon\Lambda_t/2)/(1 + \varepsilon)]$, substituted into the Callendar equation instead of R_t.

The effect due to ε, which varied slowly with time from 0 to 0.000 003, was made negligible by determining the ice point of each thermometer on each day and using this value for all temperatures computed on that day. Substitution of $(R_t - \varepsilon\Lambda_t/2)/(1 + \varepsilon)$ into the Callendar equation and cancellation of the term $(1 + \varepsilon)$ which is constant during a single day, we obtain

$$t = \frac{R_t - \varepsilon\Lambda_t/2 - R_0 + \varepsilon\Lambda_0/2}{\alpha(R_0 - \varepsilon\Lambda_0/2)} + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) \tag{32}$$

$$= \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right) - \frac{\varepsilon(\Lambda_t - \Lambda_0 R_t/R_0)}{2\alpha R_0} \tag{33}$$

In the most unfavorable case, that is $\varepsilon = .000\,003$ and $t = 444.6$, the last term has the value

$$-\frac{0.000\,003\,(5 - 4.5 \times 2.65)}{2 \times 25.5 \times 0.00392} = +\,0.0001^\circ\text{ C.}$$

This method does not correct for variations in the resistances of the mercury contacts in the commutator. The links were passed into the

cups and scrubbed back and forth several times whenever used. As far as we could determine, the variations in resistance were outside the limit of our precision, 0.000 01 ohm.

The Molecular Weight of Sulphur Vapor Along the Saturation Curve. The head of sulphur vapor in our boiling tube was approximately 35 cm. which corresponds to a pressure of about 0.1 mm. In order that the correction be known to 0.001 mm. it is necessary to know the density of saturated sulphur vapor from 660 to 860 mm. to about 1%. The volumes (liters per gram) of sulphur vapor at various temperatures and pressures are given in International Critical Tables.[14] From each entry we computed an ideal gas molecular weight M from the relation

$$M = \frac{0.08206\,(273.1 + t)}{pV}.$$

The entries in Table VII were obtained from these values by interpolation and extrapolation to pressures somewhat above the vapor pressure; and are the average of two values, one obtained by graphical smoothing and the other by numerical gradation, these values differing by less than ½%.

TABLE VII

IDEAL GAS MOLECULAR WEIGHTS OF SULPHUR VAPOR AT DIFFERENT TEMPERATURES AND PRESSURES

Pressure (atm.)	0.8	0.9	1.0	1.1	1.2
Temp. (°C.)			Molecular Weight		
430	218.2	220.7	223.2		
440	215.0	217.6	220.2	222.8	
450	211.8	214.5	217.2	219.9	222.6
460	208.5	211.3	214.1	216.9	219.7

Table VIII was then obtained by interpolation from Table VII.

TABLE VIII

SATURATION IDEAL GAS MOLECULAR WEIGHTS OF SULPHUR VAPOR

Pressure (mm.)	660	710	760	810	860
Pressure (atm.)	0.8684	0.9342	1.0000	1.0658	1.1316
Saturation Temp. (°C.)	435.00	439.94	444.60	449.03	453.25
Saturation Molecular Weight	218.3	218.5	218.8	219.3	219.8

[14] International Critical Tables, Vol. III, p. 435 (1928).

It is evident that for purposes of computation of the density of saturated sulphur vapor the ideal gas law and the average molecular weight of 218.9 will give values well within ½%.

As a check we computed the saturation molecular weight from the Clapeyron equation and data given in International Critical Tables.[15] This gave the value 220.8, which is probably only an independent check on our smoothing of the pressure-volume-temperature data for sulphur vapor.

The value $M = 219.5$ was chosen as being within 1% for the pressure range 660 to 860 mm. The density d gms. per cm.^{3} of saturated sulphur vapor over this pressure range is given by the relation

$$d = \frac{219.5\, p}{82.06\ (t + 273.1)} \tag{34}$$

where p and t are the saturation pressure (atm.) and temperature (°C.). The density so computed is independent of the ideal gas law which is used only as a smoothing function.

Reduction of the Resistance of a Platinum Resistance Thermometer to the Resistance at the Normal Sulphur Point. Let R_p be the resistance of the thermometer at the pressure p, R_{760} the resistance at the normal sulphur point, and R_o, α and δ be the constants of the thermometer. Then by substitution of Eq. (22) into Eq. (4) we obtain the expression:

$$R_{760} = R_p - \alpha R_o[(0.0908028 - 0.00716616\ \delta)\ (p - 760) - (0.000\,047573 - 0.000\,0029299\ \delta)\ (p - 760)^2 + (0.000\,000\,04361 - 0.000\,000\,002578\ \delta)\ (p - 760)^3 - 0.000\,000\,000\,00102\ \delta\ (p - 760)^4], \tag{35}$$

which holds over the pressure range 660 to 860 mm. When $\alpha = 0.003921$ and $\delta = 1.495$ this relation becomes

$$R_{760} = R_p - 0.000\,3140\ R_o(p - 760) \tag{36}$$

which introduces no error as much as 0.000 01 ohm when $(p - 760)$ is less than $\pm$ 1 mm. and when $0.003920 < \alpha < 0.003922$, $1.49 < \delta < 1.50$ and R_o is of the order of 25 ohms.

Effect of Errors in Determining R_t, R_o, α, and δ on the Computed Temperature in the Neighborhood of the Sulphur Point. Differentiation of the Callendar equation gives

[15] International Critical Tables, Vol. I, p. 102 (1926).

$$\Delta t = \frac{\Delta R_t}{R_o \alpha D} - \frac{R_t \Delta R_o}{R_o^2 \alpha D} - \frac{(R_t - R_o)\Delta\alpha}{R_o \alpha^2 D} + \left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)\frac{\Delta\delta}{D} \quad (37)$$

where

$$D = 1 - \left(\frac{2t}{100} - 1\right)\frac{\delta}{100}. \quad (38)$$

The Callendar equation is implicit in t. A change of Δt in the value of the temperature introduced into the $\delta(t/100)(t/100 - 1)$ term changes the computed temperature by

$$\Delta t = (1 - D)\Delta t. \quad (39)$$

A variation Δt_{pt} in the platinum temperature changes the international temperature by

$$\Delta t = \frac{\Delta t_{pt}}{D} \quad (40)$$

The effects of an error of 10 units in the last significant place of R_t, and in the thermometer constants R_o, α, δ on the computed temperature are given in Table IX for several equally spaced temperatures in the neighborhood of the sulphur point. Reasonable estimates of errors are: $\pm$ 0.000 02 in R_t and R_o, $\pm$ 0.000 000 025 in α, and $\pm$ 0.00020 in δ. In the determination of the effect of pressure on the sulphur point the uncertainty in R_t introduces an uncertainty in the observed temperature of 0.0002° C.; since each run is made to pass through the normal sulphur point, the uncertainties in temperature due to those in R_o, α, δ are about 0.00 01°, 0.000 08°, 0.0002° C., respectively, at 880 and 660 mm., and zero at 760 mm. The last column in Table IX gives the change in the computed temperature produced by changing t in the last term of the Callendar equation by 0.0010° C.

TABLE IX

EFFECTS OF ERRORS IN THE DETERMINATION OF R_t, R_0, α, δ ON THE TEMPERATURE COMPUTED FROM THE CALLENDAR EQUATION IN THE NEIGHBORHOOD OF THE SULPHUR POINT

$$\Delta t = \frac{\Delta R_t}{R_0 \alpha D} \qquad \Delta t = -\frac{(R_t - R_0)\Delta\alpha}{R_0 \alpha^2 D} \qquad \Delta t = (1 - D)\Delta t^*$$

$$\Delta t = -\frac{R_t \Delta R_0}{R_0^2 \alpha D} \qquad \Delta t = \left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)\frac{\Delta\delta}{D} \qquad D = 1 - \left(\frac{2t}{100} - 1\right)\frac{\delta}{100}$$

Assumed constants: $R_0 = 25.09081$ $\alpha = 0.003921378$ $\delta = 1.49251$

Assumed variations: $\Delta R_t = \Delta R_0 = 0.00010$ $\Delta\alpha = 0.000000010$

$\Delta\delta = 0.00010$ $\Delta t = 0.0010^*$

Temperature (°C. Int.)	Error × 10^3(°C.) in Computed Temperature due to				
	ΔR_t	ΔR_0	$\Delta\alpha$	$\Delta\delta$	Δt^*
454.6	1.156	−3.108	−1.249	1.833	0.121
449.6	1.154	−3.082	−1.234	1.785	0.119
444.6	1.152	−3.057	−1.219	1.737	0.118
439.6	1.150	−3.032	−1.204	1.689	0.116
434.6	1.148	−3.007	−1.189	1.643	0.115

*This equation and column give the effect on t produced by a variation in the temperature substituted into the term $\delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)$.